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Investigating the Fate of Dyes in the Environment

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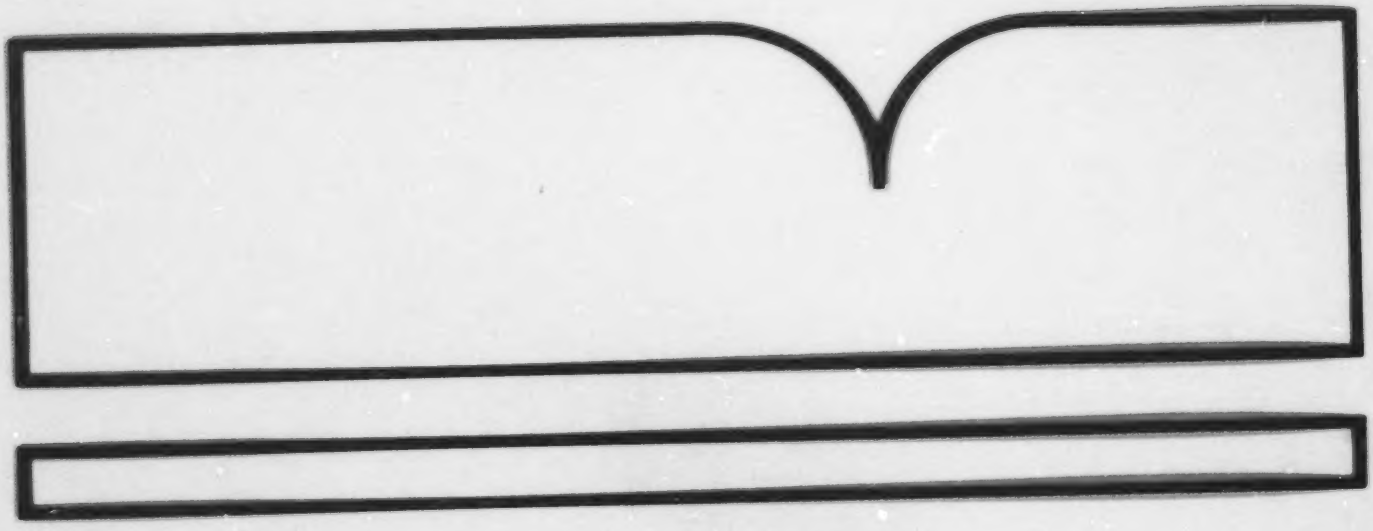

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INVESTIGATING THE FATE OF DYES IN THE ENVIRONMENT

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16. ABSTRACT

The rationale and appraoach that underlie the use of mathematical models to forecast the environmental behavior of organic chemicals are examined. The general concept are then used to show how knowledge of environmental and dye chemistry can be used to suggest pathways that are likely or unlikely to be determinants of dye fate in aquatic systems.

Reactions involving precipitation of Ca and Mg salts and ion exchange with sediments may be important for anionic and cationic dyes, respectively. The uncharged dyes are considered in regard to possible volatilization, sorption, and bioconcentration. Suitable kinetic and equilibrium constants are not currently available for quantitative prediction using mathematical models.

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INTRODUCTION

During the past 20 years, concerns about the impact of chemicals on the environment have led to the development of risk assessment procedures. The implications of such procedures are of interest and importance to manufacturers, users and regulators of chemicals used in the textile industry as well as other industries. As a class of chemicals, dyes have widespread use and wide geographical distribution. This paper describes methods that are being used to investigate the fate of organic chemicals in the environment as part of the risk assessment process. In addition, this paper addresses the benefits that may be derived from a careful analysis of the fate of dyes and of their behavior in the environment.

EXPOSURE ASSESSMENT METHODS

Currently the subject of much research is the assessment of chemical risk to the environment. In quantitative risk assessment, the two main factors considered are hazard and exposure.

Hazard describes those indicators of potential biological effects, such as toxicity, carinogenicity, etc., that are concentration and time dependent. That is, dose-response relationships determine hazard. It is important to determine whether the risk being assessed is for humans, or other specific biota, or the environment in general. Consequently, the fate of chemicals in the environment is an essential component for casting biological test results in a realistic environmental scenario for the risk assessment process.Exposure describes the expected environmental concentration of a chemical over time and distance. Exposure assessment provides the impetus for developing data on the fate of chemicals in the environment. Both hazard and exposure data, however, provide information only about what is possible. The purpose of both risk and exposure assessment is to predict what is probable.

All environmental assessments rely on both field and laboratory data. However, there may be stronger reliance on one or the other of these approaches due to specific factors. When cost and time considerations permit, field studies are usually chosen for three reasons. Field studies are often less-controversial, they can be tailored to a specific site and they can target the biota of concern. In addition, field studies have high public acceptance and credibility.

Field studies, however, are costly, time consuming, and subject to uncontrollable factors such as the amount of rainfall. Also, suitable methods for chemical and biological analysis may not be available for field studies and a defensible, explicit approach for extrapolating data or conclusions to other chemicals and sites seldom exists.

Mathematical models and laboratory data provide an alternative to field studies. When many different chemicals and sites are considered, the only practical approaches to be used are mathematical models, simulation and laboratory data collection.

Mathematical models are used to provide a first approximation of environmental concentration as an evaluative tool. The result is not expected to predict precisely the conditions found in the real environment but rather to produce a range of probable values for various scenarios. Environmental properties can be based on surveys of biota, historical records of meteorology and stream flow, or stochastic approaches. The characteristic of generality makes this approach useful and cost effective.

The objections to the use of mathematical models are a lack of confidence in the approach and doubts about the degree of accuracy required since evaluative models are best in "forecasting" generalities.

ENVIRONMENTAL BEHAVIOR OF DYES

The processes most often included in models for predicting the behavior of organic chemicals in aquatic systems are volatilization, sediment sorption, photolysis, hydrolysis, biolysis, and bioconcentration. Additional processes that may be important for dyes include ionization, abiotic oxidation, abiotic and microbial reduction, precipitation, and ligand exchange.

An important characteristic of all dyes is their ionic state; ionic compounds are, for all practical purposes, non-volatile. Therefore, volatilization should not be important for acid, direct, basic, and metal-complex dyes or for most fluorescent brightening agents. In principle, solvent, disperse, vat and sulfur dyes have the potential to be volatile. Vapor pressure data are not available for most dyes. Because sulfur dyes, vat dyes and neutral fluorescent brightening agents are large, complex molecules, however, it can be expected that they will have vapor pressures lower than disperse dyes.

A review of data in the literature in relation to vapor pressure of dyes reveals that the vapor pressures of the "older" disperse dyes are quite low. The newer, "high energy" dyes are likely to be less volatile. This conclusion, however, is based on chemical structure and not on actual vapor pressure data. Vapor pressures for several dyes and for some chemicals that have been studied in the environment are presented in Table 1.

Volatilization also is not likely to be important for the uncharged dyes because the fugacity or escaping tendency that drives volatilization is also the driving force for both sorption and bioconcentration. Because the aquatic system contains so much sorbent in the form of sediment and biomass, the rate of volatilization will be reduced in proportion to the extent that these pathways reduce the dissolved concentration. The use of fugacity to describe sorption equilibria and volatilization kinetics has been studied by Mackay (10,11). Interestingly, among the few environmental studies of dyes are two that show the occurence of these pathways. Jensen's study (7) demonstrates bioconcentration of a neutral fluorescent brightener and Tincher's report (16) shows much higher concentrations of acid and disperse dyes in sediment than in surrounding water.

Sorption of dyes will be important in the environment because dyeing itself is a sorptive process. Based on the properties of sediments, cation exchange is anticipated to be extensive and rapid for basic dyes. A similar situation should exist for acid and direct dye anions but the equilibrium constants would probably be smaller. Few studies have been done on the environmental behavior of dyes, however, for Tincher's work and some studies of anionic fluorescent brighteners.

Biolysis is often included in models for predicting the behavior of organic chemicals in aquatic systems. In relation to dyes, biolysis, whether chemically or microbially mediated, will not be fast because, if the dye is not broken down during the rigors of biological waste treatment, it is unlikely to biodegrade rapidly in the less severe conditions of the environment.

Photochemical transformation is another pathway that might be important for dyes because dyes are excellent absorbers of solar energy. Little attention has been given, however, to the study of this pathway under environmental conditions. Dyes have been designed for light fastness and Haag and Mill (6) suggest that direct photolysis will be much slower than indirect photolysis in natural waters where reactive species can form from other components such as humic materials.

Certain compounds, including dyes, are activated by light with a resulting increase in toxicity. This phenomenon was the subject of a symposium at the 192nd American Chemical Society meeting in California in 1986 on possible pesticidal applications of dyes.

Another pathway that has received little attention from environmental researchers is the reaction of organic ions. Although the scientific base exists in many cases, most models do not contain algorithms suitable for assessment. Also, few of the equilibrium constants have been published although some of these reactions are the source of problems for the dyer including reaction of ionic dyes with detergents, metals, or other dyes of opposite charge.

Some of these reactions will be operative in aquatic systems. Anionic dyes can be expected to react with Ca, Mg, etc., to form highly soluble salts and thereby reduce the concentration available for other reactions or biological effects. The effect of salt formation on solubility for a few compounds is given in Table II. Basic dyes interact with humic materials and hydrous oxides and similar results can be expected.

A related process that has implications for large organic ions is ion pair formation. However, this too has been neglected in the environmental context although its analytical applications are well known. Ion pair formation would be expected to influence any partitioning phenomenon such as bioconcentration (17). Dye molecules are excellent subjects for such studies.

The final process to be considered in investigating the fate of dyes in the environment is redox reactions. In early vat dyeing, microbial reduction was used. Also, many dyes are known to be reversibly oxidized, sometimes by air. Based on dye chemistry alone, this process will be important to the fate of certain dyes if they are present in aquatic systems. In the environment, reduction is expected to occur under anaerobic conditions that are most likely to be found in bottom sediments. The difficulty of working with anaerobic systems, however, has precluded research on the microbiology and chemistry of environmental reduction reactions.

Recently, reactions in anaerobic sediments have received attention. Abiotic reduction of nitro and azo groups have been reported (14,18,19). Studies on microbial transformation of azo dyes have been conducted but only under pure culture or waste treatment conditions. Some of the environmental questions about dyes come from the concern that azo dyes may be reduced to the starting material, for example, benzidine. Whether the formation of a small amount of a hazardous compound is more desirable than the destruction of a large portion of the dye can be objectively assessed only when kinetic, equilitrium, and biological data are available.

CONCLUSIONS

Sufficient knowledge of dye chemistry exists so that many of the reactions that determine the fate of dyes in natural waters can be defensibly identified. Most of the data on the chemistry or microbiology of dyes, however,

relate to conditions in the dye bath. Few published data exist on conditions outside of the dye bath. This is especially true of data on rate and equilibrium constants of the type needed to forecast environmental concentration and biological impacts. The most reasonable approach for obtaining information is for researchers to compile data on compounds that possess selected chemical properties. The data can then be used to predict the properties and environmental behavior of other compounds. Additional processes that may be important for dyes include ionization, abiotic oxidation, abiotic and microbial reduction, precipitation, and ligand exchange.

TABLE I. Vapor pressures (mmHg) of some dyes and other chemicals at 25 degrees C.

Compound	Vapor Pressure	Reference
1-(2-hydroxyethylamino) anthracene 9,10 dione	1.2×10^{-11}	2
4(N,N dimethylamino)azobenzene (Solvent Yellow 2) CI 11020	3.6×10^{-8}	3
4-nitro-4'-aminoazabenzene (Disperse Orange 3) CI 11005	1.9×10^{-11}	3
4(N,N dimethylamino) 5 methyl 4'nitroazabenzene	1.0×10^{-9}	3
1-methylamino-anthracene 9,10-dione (Disperse Red 9) CI 60505	1.2×10^{-8}	4
4(N-2-hydroxyethyl-N-ethylamino) 4'nitroazobenzene (Disperse Red 1) CI 11110	2.3×10^{-13}	4
1,4,5,8 tetraaminoanthracene 9,10-dione (Disperse Blue 1) CI 64500	1.8×10^{-8}	5
1,4 dihydroxyanthracene 9,10-dione	1.1×10^{-6}	5
Indigo (Vat Blue 1) CI 73000	8.3×10^{-13}	6
Mikethren Blue RSN (vat Blue 4)	1.9×10^{-18}	6
DDT	1×10^{-7}	7
Dieldrin	1×10^{-7}	7
Di(2-ethylhexyl)phthalate	2.4×10^{-7}	8

TABLE II. Effect of salt formation on solubility

Compound	Solubility (g/l)	T(C)	Ref.
1,5 anthraquinone disulfonic acid.4H2O	660	18	15
Mg 1,5 anthraquinone disulfonate.8H2O	20.4	18	16
Ca 1,5 anthraquinone disulfonate.3H2O	9.1	18	16
1,8 anthraquinone disulfonic acid .5H2O	660	18	15
Mg 1,8 anthraquinone disulfonate.6H2O	10	18	15
Ca 1,8 anthraquinone disulfonate.5 1/2H2O	0.7	18	16
2-naphthalene sulfonate	679	30	15
Mg 2-naphthalene sulfonate	69.8	17	16
Ca 2-naphthalene sulfonate	19.8	16.5	16